



## High temperature and pressure electrochemical test station

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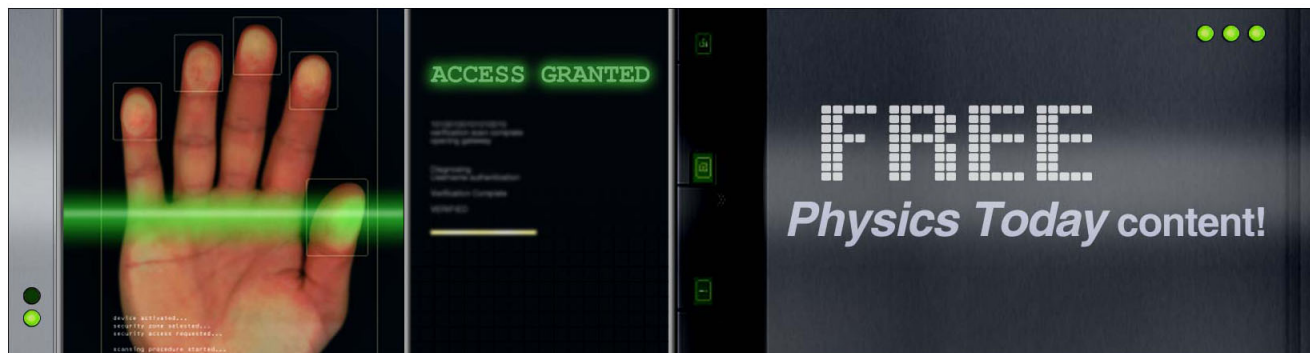
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## ADVERTISEMENT



## High temperature and pressure electrochemical test station

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An electrochemical test station capable of operating at pressures up to 100 bars and temperatures up to 400 °C has been established. It enables control of the partial pressures and mass flow of O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O in a single or dual environment arrangement, measurements with highly corrosive media, as well as localized sampling of gas evolved at the electrodes for gas analysis. A number of safety and engineering design challenges have been addressed. Furthermore, we present a series of electrochemical cell holders that have been constructed in order to accommodate different types of cells and facilitate different types of electrochemical measurements. Selected examples of materials and electrochemical cells examined in the test station are provided, ranging from the evaluation of the ionic conductivity of liquid electrolytic solutions immobilized in mesoporous ceramic structures, to the electrochemical characterization of high temperature and pressure alkaline electrolysis cells and the use of pseudo-reference electrodes for the separation of each electrode contribution. A future perspective of various electrochemical processes and devices that can be developed with the use of the established test station is provided.

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### I. INTRODUCTION

An essential ingredient of a sustainable energy system is the ability to store energy chemically. This is needed in order to provide energy for the transportation sector and in decentralized applications. It is also essential for renewable energy sources with large temporal variations, since transformation of the energy into a chemical form can ensure that the energy is available at the time when it is needed.

In this respect, it would be preferable to store the energy in a fuel that has a high energy density and is easy to handle, such as methane, methanol, or dimethylether among others. The development of an electrochemical device that can transform CO<sub>2</sub> and H<sub>2</sub>O into one of these fuels, and in that way store and recover excess renewable energy, is highly desirable. Increasing the operating pressure of such an electrochemical cell would be of great advantage as it would enhance the thermodynamic stability of the fuel, permitting operation at elevated temperatures, which is expected to promote the cell performance as most catalytic or electrochemical steps involved are thermally activated. At the same time, elevated pressure is expected to enhance the kinetics of the (electro)catalytic reactions, due to the increased impinging frequency and kinetic energy of the reacting gas molecules on the active sites.

Based on present day technology, hydrogen production through electrolysis of water is considered one of the most promising options for large scale grid storage,<sup>1</sup> as alkaline electrolysis cells (AECs) represent a very mature technology, with a number of companies being active in the field and having demonstrated MW-scale systems with stable operation for many years.<sup>2</sup> The milestone report published by the National

Renewable Energy Laboratory (NREL)<sup>3</sup> suggests that electricity costs comprise 80% of the total selling price of hydrogen from large-scale electrolyzers, which emphasizes the need for improvement in their electrical energy efficiency. This can be achieved by raising the operating temperature and pressure.

A cleaner and more sustainable way to produce ammonia, as compared to the Haber-Bosch process used today, is one of the biggest chemical challenges of our days. An electrochemical cell, with a proton conducting electrolyte, that combines N<sub>2</sub> and H<sub>2</sub>O into NH<sub>3</sub> (and O<sub>2</sub>) could help reduce the environmental cost of the Haber-Bosch process. Pressurized operation could also be of great benefit in this case as it would improve the thermodynamic stability of NH<sub>3</sub> and the reaction kinetics.

To achieve the type of cells described above, development of new materials for use as electrolyte and (electro)catalysts is necessary. Investigation of materials properties under high pressure and temperature and in varying gas compositions is required, as well as fabrication and testing of electrochemical cells. To enable this type of research, we have designed, constructed, and demonstrated a high pressure and temperature electrochemical test station, that (i) can operate up to 100 bars and 280 °C (potentially up to 400 °C when the Teflon components are removed), (ii) possesses a series of electrochemical cell holders capable to accommodate different types of cells, (iii) enables control of the O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O partial pressures in a single or dual environment arrangement, (iv) permits localized gas sampling and analysis, and (v) can accommodate and electrochemically characterize multiple cells simultaneously, e.g., by electrochemical impedance spectroscopy, cyclic voltammetry, galvanostatic or potentiostatic tests.

A number of high temperature and pressure electrochemical cell stations have been demonstrated up to day for

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TABLE I. Type and specifications of the main gas handling components utilized in the construction of the high temperature and pressure electrochemical test station. The utilized abbreviations stand for: MFC = mass flow controller, CB = catalytic burner, MV = magnetic valve, G = gas sensor, PS = pressure sensor, PCV = pressure control valve, ET = electro-pneumatic transducer, PRV = pressure reduction valve, R = pressure relief valve, PV = pneumatic on/off valve, GLS = gas/liquid separator, PID = proportional integral derivative.

Component	Model	Characteristics
MFC	Brooks SLA5850	Max flow = 0.5 NI/min, $P < 100$ bars, $2 \text{ bars} < DP < 98$ bars, Gas type: $\text{N}_2/\text{CO}_2/\text{O}_2/\text{H}_2$
CB	Süd-Chemie catalyst type FCCB-ENV1	Catalyst loaded on a 1 in. $\times$ 2 in. $\text{ZrO}_2\text{-Al}_2\text{O}_3$ ceramic monolith support with 400 cpsi
MV	Bürkert type 2200	Max flow = 33 NI/min, $P < 250$ bars, $T < 130^\circ\text{C}$ , Gas type: $\text{N}_2/\text{CO}_2/\text{O}_2/\text{H}_2$
G	Geopal type GP-SA, GP-CO, and GJ-O2	Gas type: $\text{H}_2$ , CO, and $\text{O}_2$ , respectively
PS	Schneider Electric type XMLP100BD22	$P$ range = 0–100 bars, $T < 120^\circ\text{C}$
PCV	Badger type 859 valve with type 754 actuator	Max flow = 10 NI/min, $P < 250$ bars at $T \leq 400^\circ\text{C}$ , Gas type: $\text{N}_2/\text{CO}_2/\text{O}_2/\text{H}_2/\text{H}_2\text{O}$
ET	ControlAir type 500X	
PRV	Linde type R200/1	Inlet $P < 230$ bars, $T < 50^\circ\text{C}$
R	Swagelok type R3A-C	$P < 413$ bars, Set $P = 100$ bars, $T < 150^\circ\text{C}$ , Gas type: $\text{N}_2/\text{CO}_2/\text{O}_2/\text{H}_2/\text{H}_2\text{O}$
PV	Swagelok SS-HBVS4-O	$P < 165$ bars, $T < 204^\circ\text{C}$ , Gas type: $\text{N}_2/\text{CO}_2/\text{O}_2/\text{H}_2/\text{H}_2\text{O}$
GLS	Delta Plus coalescing filter	$P < 100$ bars, $T < 60^\circ\text{C}$ , Element: borosilicate glass fibres
PID	Eurotherm type 2216e	
Glands	Conax TG-24(K)-A4-T	$P < 303$ bars, $T < 232^\circ\text{C}$ , Gas type: $\text{N}_2/\text{CO}_2/\text{O}_2/\text{H}_2/\text{H}_2\text{O}$

alkaline electrolysis cells,<sup>4–6</sup> solid oxide cells,<sup>7</sup> and  $\text{CO}_2$  electrolysis cells using aqueous solutions<sup>8–10</sup> among others, but they lack the versatility and extended range of operating conditions of the test station reported here. To achieve this kind of functionality, a series of safety and engineering design challenges had to be addressed. It is the intention of this publication to provide a comprehensive description of the developed test station, with emphasis on electrochemical cell holder design and safety considerations. Furthermore, a few selected examples of materials and electrochemical cells examined are also provided.

## II. DESCRIPTION OF TEST STATION

### A. Gas handling

The test station consists of a vented gas handling cabinet (GHC) which houses all the gas handling equipment, such as mass flow controllers (MFC), a ball flow meter (BFM), catalytic burners (CB), magnetic valves (MV), gas sensors (G), pressure sensors (PS), manometers (P), a pressure control valve (PCV), an electro-pneumatic transducer (ET), pressure reduction valves (PRV), a pressure relief valve (R), check valves (C), on/off and 3-way valves (V), needle valves (NV), and a gas/liquid separator (GLS). A list of the most important gas handling components used is given in Table I. It also houses a furnace with multiple thermocouples, an autoclave with multiple thermocouples and wire throughputs (glands) for electrochemical measurements, proportional integral derivative (PID) controllers for electronic control of temperature and pressure, a safety surveillance system and a computer system which handles temperature, gas flow, and pressure management as well as data acquisition.

All the gases to the setup are supplied from 200 bars bottles which are placed outside the laboratory. The pressure is reduced to 100 bars outside the laboratory and gases are subsequently piped to the wall panel inside the laboratory. Figure 1 gives an overview of the gas handling system of

the test station. In the MFCs, the pressure is reduced to the test pressure in the autoclave, which is adjusted by the PCV. Downstream the PCV the pressure is near atmospheric.

### B. Management of gases to the autoclave

Each gas channel is equipped with PRVs, such that the inlet pressure can be adjusted to the desired value in the range 10–100 bars. Manual shutoff valves enable the test station to be completely dismantled from the main gas supply. A needle valve is used in the case of  $\text{O}_2$  (NV-03B) to assure that the pressure will increase gradually once the valve is opened. In addition, each gas channel is equipped with a computer controlled MV that allows an automated selection of the gases that will be supplied to the autoclave as well as immediate shutoff of all gas streams in case of an alarm. All gas channels are equipped with MFCs. The maximum inlet gas flow to the autoclave is determined by the maximum flow of the MFCs, specified in Table I. To avoid accidental mixing of gases, each gas line is equipped with a check valve which prevents back flow. Analog manometers (P-01–P-04) installed before the MFCs indicate the gas pressure in the inlet pipes. The gas lines that may contain  $\text{CO}_2$  at pressures above 73 bars are heated to about  $50^\circ\text{C}$  to avoid condensation of  $\text{CO}_2$ . Two manual on/off valves (V-03C and V-04C) allow for manual ventilation of the  $\text{O}_2$  and  $\text{H}_2$  lines, respectively.

The gases enter the autoclave via three inlet ports, numbered 3, 5, and 7 in Figure 1. Two of them (3 and 7) are fed directly to a CB. Inert ( $\text{N}_2$ ,  $\text{CO}_2$ ) and oxidizing gases ( $\text{O}_2$ ) are fed through one pipeline (inlet 3) and explosive gases ( $\text{H}_2$ ) are fed through the second (inlet 7). The CB comprises a honeycomb structured  $\text{ZrO}_2\text{-Al}_2\text{O}_3$  ceramic body loaded with a catalyst (from Süd-Chemie) that permits combustion of  $\text{H}_2$  at temperatures below its self-ignition temperature, even at room temperature (see Sec. III A and Appendix A). The CB at the inlet (CB-01) allows the user to control the water vapor pressure of the inlet gas, by burning  $\text{H}_2$  and  $\text{O}_2$  at the user

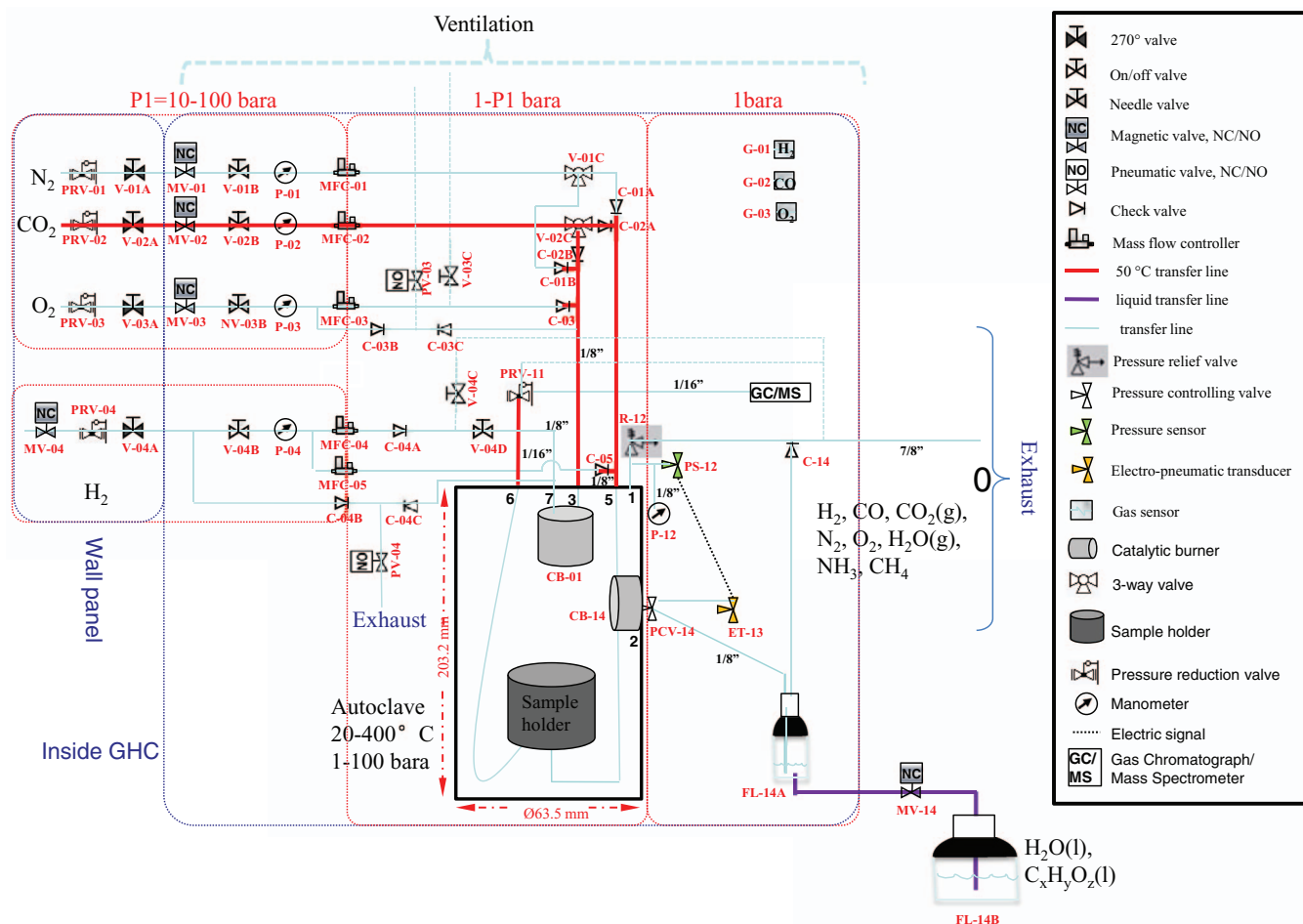


FIG. 1. Gas handling diagram of the high temperature and pressure test station. The entire test station is placed inside a vented gas handling cabinet (not shown).

specified flow rate. The test station is intended for H<sub>2</sub>O electrolysis experiments, among others, during which H<sub>2</sub> and O<sub>2</sub> is produced. A second CB placed right before the outlet of the autoclave (CB-14), ensures that the produced H<sub>2</sub> and O<sub>2</sub> will recombine into H<sub>2</sub>O. Good performance of the two catalytic burners is important, as they guarantee that an explosive mixture of H<sub>2</sub> and O<sub>2</sub> will not be formed. Their performance was thus carefully examined and the results are summarized in Appendix A.

Inlet port 5 offers the possibility to supply inert (N<sub>2</sub>, CO<sub>2</sub>) and explosive gases (H<sub>2</sub>) into the autoclave, allowing for testing of button cells with N<sub>2</sub>, CO<sub>2</sub>, and/or H<sub>2</sub> supply to one electrode and H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, and/or N<sub>2</sub> to the other. This is achieved using the electrochemical cell holders described in detail below, which allow for simultaneous testing of up to four button cells. Steam can only be supplied through inlet 3 and 7, and not through inlet 5. Also, N<sub>2</sub> and CO<sub>2</sub> cannot be supplied simultaneously through both inlet 3 and 5.

### C. Management of gases from the autoclave

The exhaust gases from the autoclave exit via a single outlet (port number 2). The pressure control valve (PCV-14), placed right after port 2, regulates the flow rate of the exhaust gas to achieve the desired pressure in the autoclave. The pres-

sure of the exhaust gas is reduced to almost atmospheric pressure after the PCV-14. The exhaust gas is then delivered to a water cooled steel bottle (condensation bottle) in order to condense the water vapor present in the exhaust gas stream, and then further piped out of the laboratory building. A pressure relief valve (R-12) is installed on outlet port 1. The valve will open and release gas if the pressure in the autoclave exceeds 100 bars. A capillary tube is also installed inside the autoclave (outlet port 6) and can be freely positioned close to either electrode of an electrochemical cell. The capillary tube can deliver small amounts of gas to a gas chromatograph or mass spectrometer (MS) for gas analysis. A pressure reduction valve (PRV-11) reduces the electrochemical cell gas pressure to almost atmospheric pressure before it is delivered to the gas analysis instrument. A more detailed description of the gas sampling system is provided below.

### D. Pressure management

The pressure in the autoclave can be adjusted automatically by a computer operated pressure control system. This consists of the pneumatic pressure control valve (PCV-14) and an electro-pneumatic transducer (ET-13), which is guided by the signal of the pressure sensor (PS-12) and a PID controller (not shown in Figure 1). The pressure relief valve



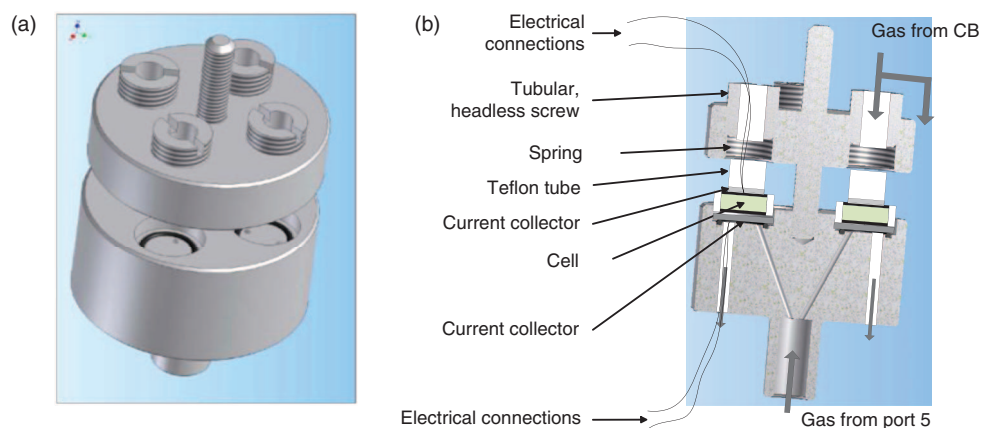


FIG. 2. (a) Top-side view and (b) cross section of electrochemical cell holder for testing multiple button cells.

(R-12) will open if the autoclave pressure increases above 100 bars and will close again when the pressure drops below 100 bars. Moreover, the pressure in the main gas supply lines is reduced to 100 bars before it enters the laboratory which assures that the gas flow to the autoclave will stop when the pressure in the autoclave reaches 100 bars.

## E. The autoclaves

### 1. Autoclave 1

The main body of the autoclave is cylindrical (48 mm inner diameter and 280 mm length) and constructed from 6 mm thick steel. A Ti liner offers increased corrosion resistance to the inner part of the autoclave. A Teflon liner is also placed inside the autoclave for further resistance to corrosion in severe chemical environments, such as aqueous KOH or  $\text{KHCO}_3$ . The autoclave possesses a lower and an upper lid, made of Inconel 625, with openings for gas inlets/outlets and wire throughputs. Teflon seals are used in the throughputs and Teflon insulated K-type thermocouple wires. Sealing between the autoclave body and the lids is achieved using O-rings of Ti or Teflon and by tightening a number of bolts. Teflon decomposes at  $327^\circ\text{C}$  and therefore the temperature inside the autoclave is not permitted to exceed  $280^\circ\text{C}$  such that Teflon parts are not damaged. Nevertheless, the autoclave can operate up to  $400^\circ\text{C}$  when removing the Teflon liner and replacing the wire insulation with glass or ceramic fiber insulation. The bolts are made of a steel composition with a smaller thermal expansion coefficient than that of the autoclave body, which offers increased tightening and better quality sealing with increasing temperature. The autoclave has been tested hydrostatically to pressures up to 200 bars.

### 2. Autoclave 2

This is a Parr Type 4760 cylindrical autoclave (64 mm inner diameter and 203 mm length). It is made of Inconel 600 and possesses a polytetrafluoroethylene (PTFE) liner for increased corrosion protection. The maximum working pressure specified by the manufacturer is 200 bars and the autoclave has been tested hydrostatically to pressures up to 289 bars. This autoclave has only one upper lid that possesses

all the feed-throughs for gases and wires. Teflon seals are used in the wire throughputs and K-type thermocouple wires. Sealing between the autoclave body and the lid is achieved using a Teflon O-ring and by tightening a number of bolts. This autoclave can be operated up to  $350^\circ\text{C}$  when removing the Teflon liner and wire insulation.

## F. The heating system

The heating system for autoclave 1 comprises two heating elements which are in direct contact with the autoclave body. Autoclave 2 is heated by a 780 W heating jacket supplied from Parr. Alumina wool is wrapped around the autoclaves to thermally insulate them from the surroundings. The furnaces are computer controlled using PID controllers. A surveillance system prohibits the temperature to increase above  $280^\circ\text{C}$ . The upper limit can be raised to 350 or  $400^\circ\text{C}$  when removing the Teflon components from inside the autoclaves. Under operating conditions, the temperature of the surroundings near the autoclaves does not exceed  $50^\circ\text{C}$ .

## G. Electrochemical cell holders

### 1. Multiple button cells holder

An electrochemical cell holder for testing up to four button cells simultaneously has been constructed using Inconel 625 (Figure 2). A tubular headless screw is used to fix each cell. A Ni spring ensures that the metallic mesh (Pt or Ni) current collector, which is wrapped around a PTFE tube, has good contact with the upper electrode of the cell. A metallic mesh is also used as current collector at the lower electrode side. Each cell is pressed on a PTFE O-ring that prohibits gas mixing between the lower and upper electrodes, thereby enabling testing in a dual environment arrangement.

### 2. Single button cell holder with reference electrode fixture

A single button cell holder with a fixture for a reference electrode was constructed using two Inconel 600 tubes and a PFA (Perfluoroalkoxy) Swagelok type PFA-820-6 fitting, as shown in Figure 3. Nitinol (Ni-Ti alloy) tension springs

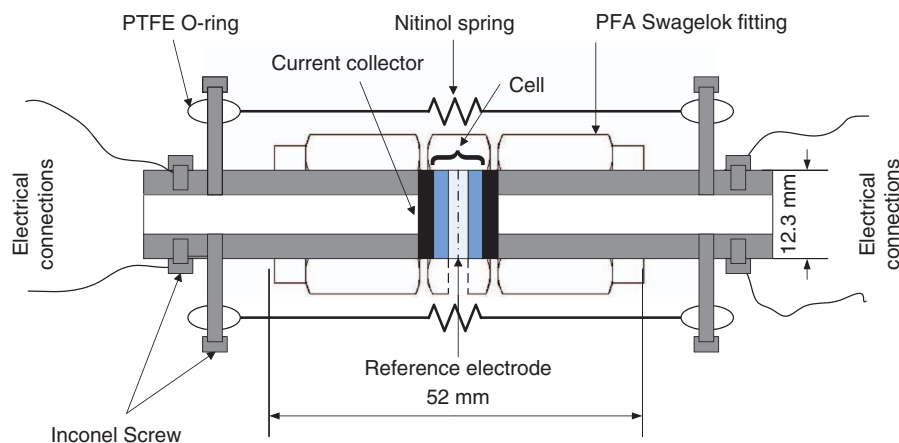


FIG. 3. Electrochemical cell holder for testing a single button cell with reference electrode.

apply a constant force between the two Inconel tubes which act as current collectors. Inconel screws attached on the Inconel tubes act as connection points and as anchoring points for the Nitinol springs. PTFE rings ensure electronic insulation between the Inconel screws and the Nitinol springs. The electrochemical cell is placed between the two Inconel tubes. A reference electrode can be connected through a 5 mm diameter hole on the side of the PFA fitting.

### 3. Multiple immobilized liquid electrolyte cells partly immersed in liquid electrolyte

An electrochemical cell holder has been constructed for testing up to four cells with immobilized liquid electrolyte, offering the possibility to have the cells partly immersed in the liquid electrolyte. The electrochemical cell holder is made of Teflon and Inconel 625, as shown in Figure 4. The Teflon container is partly filled with the required electrolyte. The cells are positioned near the upper part of the holder and fixed in place with a screw, in a manner similar to that depicted in Figure 2(b). Each cell is pressed on the flat face of the protruding PTFE piece at the center of the holder, and thus the two electrodes are hermetically separated and the cells can be tested in a dual environment arrangement.

### 4. Holders for liquid and immobilized liquid electrolyte conductivity measurements

The electrochemical cell holder for measuring the conductivity of a liquid electrolyte using the van der Pauw technique<sup>11,12</sup> is shown in Figure 5(a). Pt black coated Pt wires are placed on the sides of a PTFE beaker and kept in place by a PTFE pellet at the bottom and a PTFE wire at the outer top of the electrochemical cell holder. A PTFE lid with a 3 mm diameter orifice in the center helps retain the height of solution constant and minimize evaporation or condensation.

Figure 5(b) depicts the cell holder developed for van der Pauw conductivity measurements of immobilized liquid

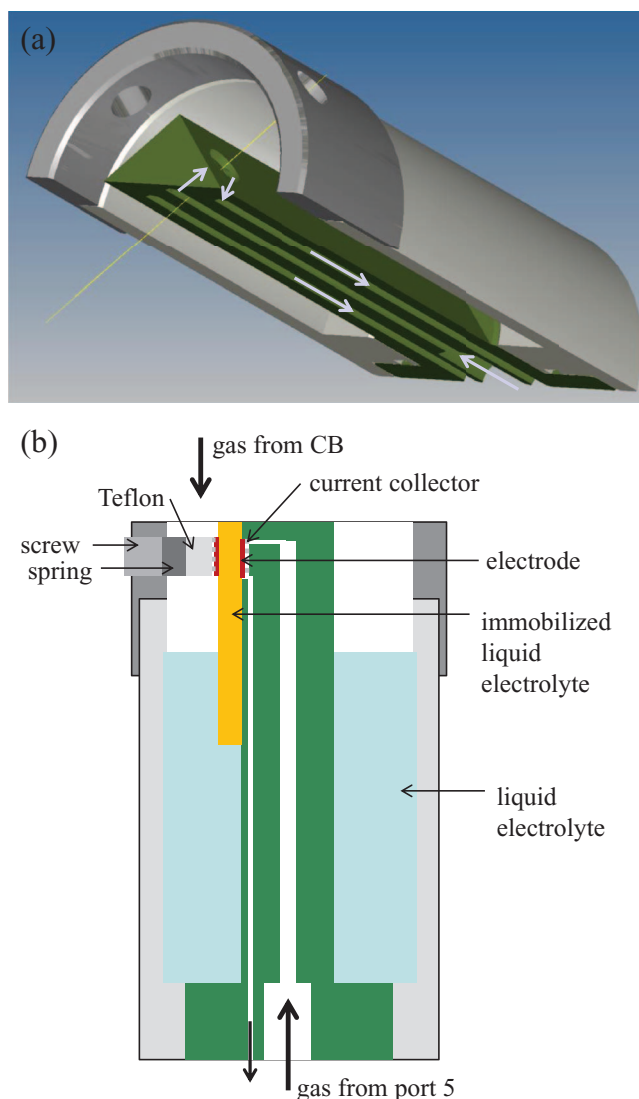


FIG. 4. (a) Top-side view and (b) side view of the cross section of the electrochemical cell holder for multiple cells with immobilized liquid electrolyte potentially immersed (partly) in the liquid electrolyte. The arrows mark the flow of gas to and from the inner electrode.

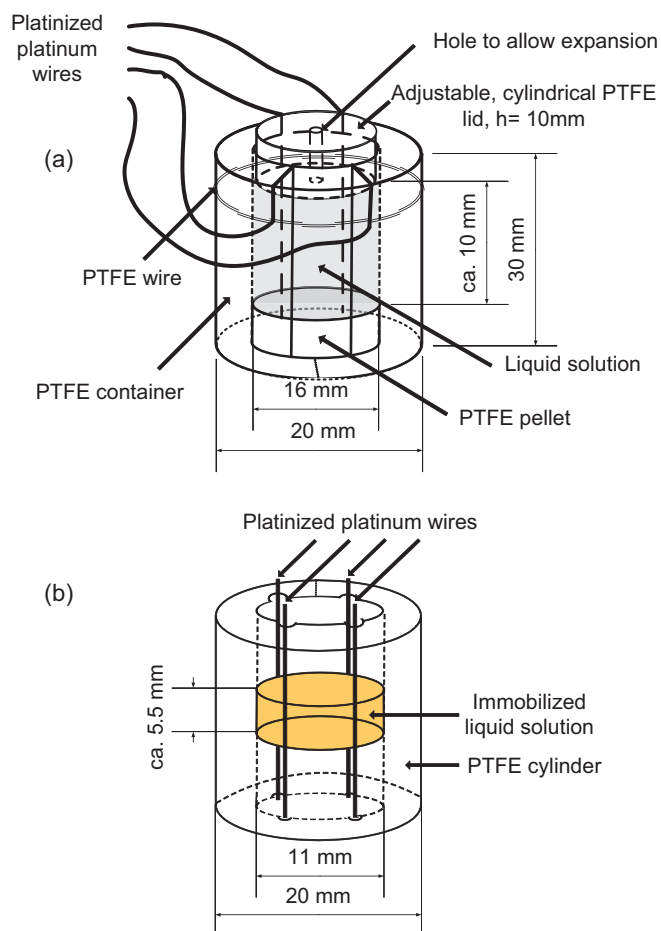


FIG. 5. Cell holders for measuring the conductivity of (a) liquid solutions and (b) immobilized liquid solutions using the van der Pauw technique.<sup>11,12</sup>

electrolytes. A slit in the tubular PTFE body of the holder allows some flexibility in the cell diameter. Pt black coated Pt wires are used again as electrodes and kept in place by PTFE wires at the outer top and bottom of the cell holder.

## H. The gas analysis system (GAS)

As shown in Figure 1, the autoclave can be connected to a GAS through port 6. A more detailed description of the gas line designed for this purpose is provided here, and illustrated in Figure 6. Valve V-11A enables the operator to feed the GAS with gas from the autoclave. The gas/liquid separator (GLS-11) will condense and separate any liquids from the gas stream. It comes with a manual valve V-11C that enables the user to collect (and potentially analyze) the accumulated liquid. Prior to emptying the GLS, V-11A is closed, and  $N_2$  is flushed through the line, by opening valves V-11B and V-11F, which are normally closed. Valves V-11D and V-11E are normally open. The pressure reduction valve (PRV-11) reduces the pressure from the autoclave pressure to about 1 bar. A ball flowmeter is connected downstream the PRV and enables manual control of the flow to the gas analysis system. When a gas chromatograph is used, a flow of the order of a few Nml/min is required through the instrument. In this case, valve V-11G is closed. When a MS is used V-11G is opened, as in this case there is only a discontinuous flow of a few  $\mu\text{l/min}$  through the instrument. A check valve (C-11A) is used to ensure that the MS will not be damaged if the operator forgets to open valve V-11G, as it ensures that the overpressure at the MS inlet will not exceed 340 mbar. All gas outlets are connected to the exhaust of the test station.

## I. The condensation bottle

The condensation bottle (500 ml volume) is equipped with a series of upper and lower level sensors. A magnetic valve (MV-14 in Figure 1) opens automatically to empty the water bottle when the water level reaches the upper water level limit and closes when the water level reaches the lower water level limit. This ensures that the condensation bottle does not overflow with water or empty completely from water, which would allow potentially explosive or toxic gases to

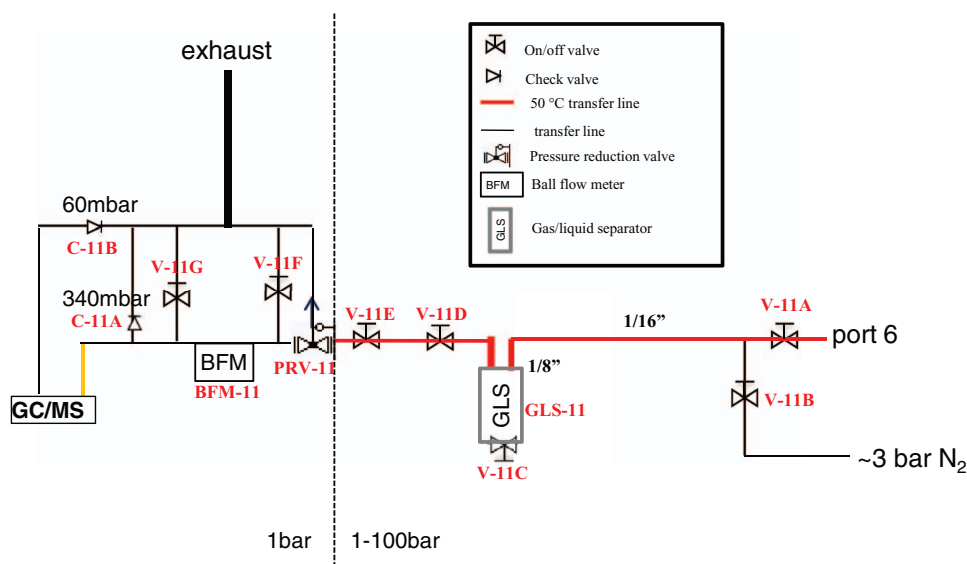


FIG. 6. Connection of the capillary tube from the autoclave (port 6) to the gas analysis instrument (GC/MS).



escape from the bottle. The water level sensing is achieved by applying 5 V dc between a long Pt wire (L1) and five other Pt wires of different lengths placed inside the condensation bottle. When both L1 and another Pt wire are immersed in water, electrolysis will take place. A 600 k $\Omega$  resistor is connected in series and the voltage drop on this resistor is used as an indicator of the water level. Due to the presence of the 600 k $\Omega$  series resistor, the electrolysis current is limited to below 10  $\mu$ A. The water level sensing is performed periodically every 1 h in order to exclude the possibility of accumulating O<sub>2</sub> (produced electrolytically during sensing) above the upper explosion limit when the condensation bottle is filled with H<sub>2</sub>.

### III. SAFETY CONSIDERATIONS

#### A. Gas types

##### 1. Explosive gases

H<sub>2</sub> and CO are explosive gases. Moreover, CO is toxic in very small concentrations and is therefore discussed in Sec. III A 2. Mixtures of H<sub>2</sub> and air at 1 bar and room temperature may ignite when the H<sub>2</sub> concentration is between 4.1 and 74.4 vol.%.<sup>13</sup> The corresponding values for mixtures of H<sub>2</sub> and O<sub>2</sub> are 4.0 and 95.2 vol.%, respectively.<sup>13</sup> Thus, 4 vol.% is referred to as the lower explosion limit (LEL) for H<sub>2</sub>. Depletion with an inert gas insignificantly affects the LEL. The LEL decreases almost linearly with increasing temperature but the temperature dependence is very weak ( $-0.003$  vol.%/K).<sup>13</sup> The self-ignition temperature in air is about 500 °C at 1 bar pressure.<sup>14</sup> The LEL of H<sub>2</sub> increases with increasing pressure.<sup>13</sup> Between 1 and 100 bars, the LEL of H<sub>2</sub> is in the range of 4–5.7 vol.% at 20 °C. Any leakage of H<sub>2</sub> inside the GHC will be detected by a gas sensor (G-01 in Figure 1) placed in the GHC. H<sub>2</sub> leaking outside the GHC will be detected by gas sensors in the laboratory building.

##### 2. Carbon monoxide

CO is toxic in very small concentrations and the hygienic limit (HGV) is 25 ppm.<sup>15</sup> The LEL of CO in air is 12 vol.%<sup>16</sup> and therefore, in this context, it suffices to handle CO as a toxic gas. Any leakage within the GHC will be detected by a CO gas sensor (G-02 in Figure 1) placed in the GHC. CO leaking outside the GHC will be detected by gas sensors in the laboratory. All the sensors are connected to the safety system.

##### 3. Carbon dioxide

CO<sub>2</sub> is colorless and at low concentrations it is also odorless. At higher concentrations it has a sharp, acidic odor. When inhaled at concentrations much higher than usual atmospheric levels, it can produce a sour taste in the mouth and a stinging sensation in the nose and throat. Concentrations above 5000 ppm are considered unhealthy,<sup>15</sup> and above 5 vol.% life threatening. The level of CO<sub>2</sub> in the GHC is not monitored as it cannot rise above 2000 ppm, on the basis of

the maximum flow rate of CO<sub>2</sub> that can be delivered in the GHC (0.5 NI/min) and the flow rate of the cabinet ventilation (250 NI/min).

At  $-78.51$  °C and atmospheric pressure, CO<sub>2</sub> passes directly from the solid phase to the gaseous phase through sublimation, or from gaseous to solid through deposition. The triple point of CO<sub>2</sub> is at about 5.2 bars and  $-56.6$  °C. The critical point is at 73.8 bars and  $31.1$  °C.<sup>17</sup> To avoid CO<sub>2</sub> condensation, transfer lines carrying CO<sub>2</sub> at pressures potentially exceeding 73 bars are heated to approximately 50 °C.

#### 4. Oxygen

High pressure O<sub>2</sub> can react violently with common materials such as oil and grease. Other materials may catch fire spontaneously. Nearly all materials including textiles, rubbers, and metals will burn vigorously in oxygen. Even a small increase in the oxygen level to 24 vol.% can create a dangerous situation. It becomes easier to start a fire, which will then burn more fiercely than in atmospheric air. To assure that the oxygen activity in the GHC does not significantly exceed the oxygen activity in air (i.e., does not exceed 0.23), the oxygen concentration of the gas in the GHC is monitored with a gas sensor (G-03). All gas handling components along the O<sub>2</sub> line are approved for use with O<sub>2</sub>. Teflon, which is used for sealing and corrosion protection in the autoclave, has an auto-ignition temperature of 435 °C at 103 bars O<sub>2</sub> pressure,<sup>18</sup> and its use is therefore considered safe.

#### B. The safety system

The safety system surveys the gas in the GHC and in the building to assure that the explosive, oxidizing, or toxic gases H<sub>2</sub>, O<sub>2</sub>, or CO, respectively, do not accumulate to explosive, highly oxidizing, or health threatening levels. Furthermore, the safety system surveys the pressure and temperature in the autoclave to assure the maximum permissible values are not exceeded. A list of the parameters and alarm limits monitored by the safety system is provided in Table II. The sensors that monitor these parameters are connected to the safety unit.

If any of the monitored signals exceeds the safety limit, the safety unit will set the test station into safety mode, i.e., interrupt the gas supply to the test station, shut off the power supply to the furnace, vent the autoclave and the H<sub>2</sub> and O<sub>2</sub> lines, and trigger a visual alarm. The PCV is of the type “normally open” (NO) and permits a maximum flow rate of 10 NI/min, which allows the autoclave to be vented within less than 5 min. A manual switch, placed outside the laboratory, enables setting the test station in safety mode from outside the building. A manual switch with a similar function is also attached outside the GHC of the test station.

The front panel of the safety unit has a series of green and a series of red LEDs for each parameter monitored. If the signal value for a given parameter is within the specified range, the green LED is lit and if the signal value is outside the specified range the red LED is turned on. All sensor signals are logged by the computer system. If a parameter escapes

TABLE II. Parameters and alarm limits monitored by the safety unit and safety action.

Signal limit/sensor	Action
Autoclave temperature < 280 °C/Thermocouple type K permanently mounted inside the autoclave.	Assures that the autoclave temperature does not exceed the maximum permissible value.
Autoclave pressure < 97 bars/Schneider electric type XMLP100BD22	Assures that the pressure in the autoclave does not exceed the maximum permissible value.
CO concentration < 20 ppm/Geopal type DET-5003	Assures that the concentration of CO in the GHC does not exceed the threshold limit value.
H <sub>2</sub> concentration < 10% LEL/Geopal type DET-5000	Assures that the concentration of H <sub>2</sub> in the GHC does not exceed 10% of the LEL.
19 vol.% < O <sub>2</sub> concentration < 23 vol.%/Geopal type DET-5004	Assures that the O <sub>2</sub> activity in the GHC remains within safety limits.
Ventilation speed in GHC > 0.83 m/s/Flow sensor Weber type 3202.30/5/24V DC mounted in the ventilation pipe that has a diameter of 80 mm	Assures that the ventilation flow in the GHC does not drop below 15 N m <sup>3</sup> /h.
Door of GHC closed/Magnetic contact Aritech type DC101	Assures that the door of the GHC is not opened by accident. A safety key can overrule this.

the permitted range and thereby activates the safety mode, the safety unit can only be reset manually by pressing a “reset” button before the test station can return to normal operation.

A risk assessment of the test station has been undertaken and can be found in Appendix B. It lists a number of possible incidents and failures in the test station, their potential consequences, and how the safety system responds to warrant safety.

#### IV. EXPERIMENTAL EXAMPLES

##### A. Electrical conductivity of aqueous and immobilized KOH

The conductivity of aqueous KOH and aqueous KOH immobilized in mesoporous SrTiO<sub>3</sub> was investigated at elevated pressures and temperatures using the van der Pauw method<sup>11</sup> in combination with electrochemical impedance spectroscopy (EIS) with the help of the cell holders shown in Figure 5. The temperature dependence of the conductivity is plotted in Figure 7 for 35, 45, and 55 wt.% KOH. Values as high as 2.9 S cm<sup>-1</sup> and 0.84 S cm<sup>-1</sup> were measured at 200 °C for 45 wt.% aqueous and immobilized aqueous KOH, respectively.<sup>19</sup> The measurements were carried out at elevated pressures of 25–40 bars in humidified N<sub>2</sub>, to ensure that the KOH solution would remain in the aqueous phase and retain its concentration at elevated temperatures.

The development of thermally stable and chemically inert mesoporous structures that can retain concentrated aqueous KOH at elevated temperatures is a major breakthrough, as it enables the production of AECs capable of operating at high temperatures.<sup>20</sup> Optimizing the ionic conductivity of such mesoporous membranes by optimizing the porosity, pore size, matrix composition, and thickness is crucial and the electrochemical test station presented here can facilitate this development effort. Furthermore, the ionic conductivity of other solutions at elevated temperatures and pressures and under controlled environments can be investigated.

##### B. Full cell and single electrode characterization

In order to realize efficient electrochemical devices operating at elevated temperatures and pressures, extensive work is needed in the development of active, selective, stable, and cheap electrode materials and microstructures. In order to expedite this effort, the electrochemical cell holder presented in Figure 2 has been constructed that enables characterization of up to four button cells at the same time. This enables testing of different materials and microstructures simultaneously and under identical conditions, as well as nominally identical cells in order to establish reproducibility.

As an example, the *i*-V characteristic and EIS at 1.5 V applied cell voltage of an AEC operating at 200 and 250 °C at 40 bars is shown in Figure 8. The cell was made of a thick mesoporous SrTiO<sub>3</sub> layer where 45 wt.% aqueous KOH electrolyte was immobilized, and metal foam based electrodes. Inconel foam with dispersed Mo was used for the H<sub>2</sub> evolution electrode and Ni foam with added Co for the O<sub>2</sub> evolution

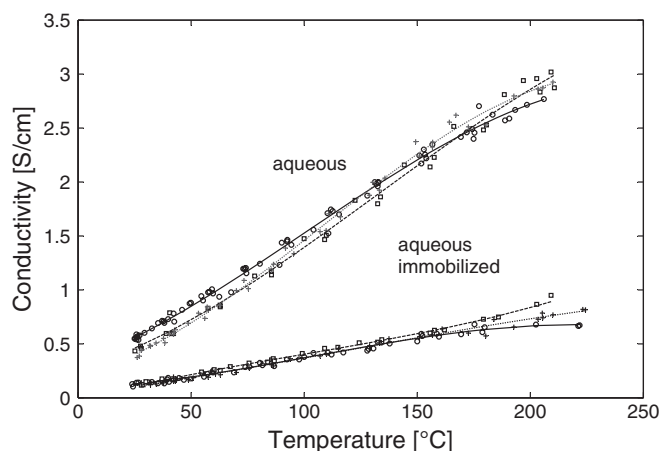


FIG. 7. Conductivity of 35 (○), 45 (□), and 55 (+) wt.% aqueous KOH and aqueous KOH immobilized in mesoporous SrTiO<sub>3</sub> as a function of temperature in 25–40 bars humidified N<sub>2</sub>. The measurements were conducted using the cell holders shown in Figure 5.

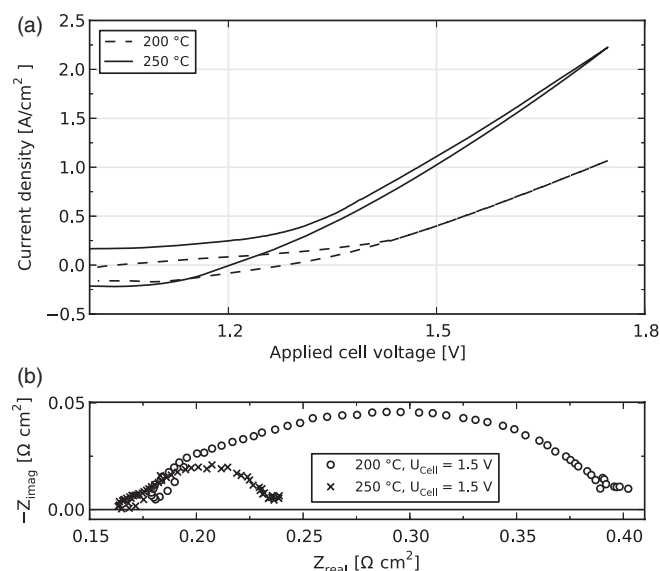


FIG. 8. (a) i-V and (b) EIS at 1.5 V applied cell voltage for an AEC operating at 200 and 250 °C at 40 bars. The cell consisted of Mo activated Inconel foam cathode, 45 wt.% aqueous KOH immobilized in mesoporous  $\text{SrTiO}_3$  as electrolyte, and Co activated Ni foam anode. The cell testing took place in the multiple button cells holder illustrated in Figure 2.

electrode. A current density of  $1.1 \text{ A}/\text{cm}^2$  and  $2.3 \text{ A}/\text{cm}^2$  was obtained at a cell voltage of 1.5 V and 1.75 V, respectively, when operating at 250 °C and 40 bars. The drastic improvement in cell performance by increasing the operating temperature can be clearly seen in Figure 8(b). The area specific electrode polarization resistance decreased by a factor of 3 from 220 to  $70 \text{ m}\Omega \text{ cm}^2$  by increasing the temperature from 200 to 250 °C.<sup>21</sup>

To further facilitate the electrode development work, it is necessary to be able to separate the contribution of each electrode in the total electrode polarization resistance. This can be achieved with the use of the electrochemical cell holder presented in Figure 3, which possesses a fixture for the

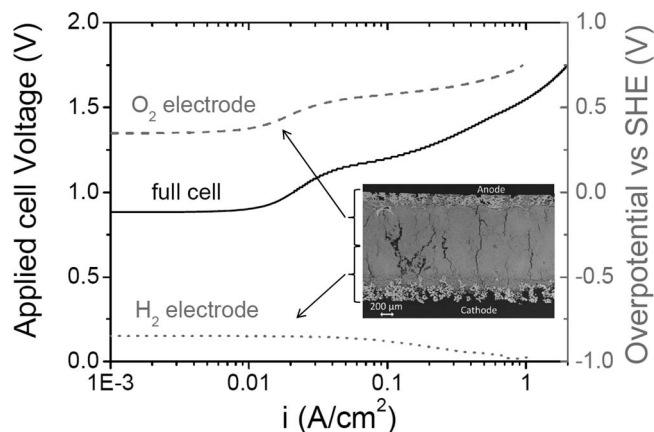


FIG. 9. Applied cell voltage and electrode overpotentials (vs SHE) as a function of current density for an alkaline electrolysis cell operating at 250 °C and 42 bars. The cell consisted of Inconel foam cathode, 45 wt.% aqueous KOH immobilized in mesoporous  $\text{SrTiO}_3$  as electrolyte, and Ag activated Ni foam anode. The cell testing took place in the single button cell holder possessing a reference electrode fixture shown in Figure 3.

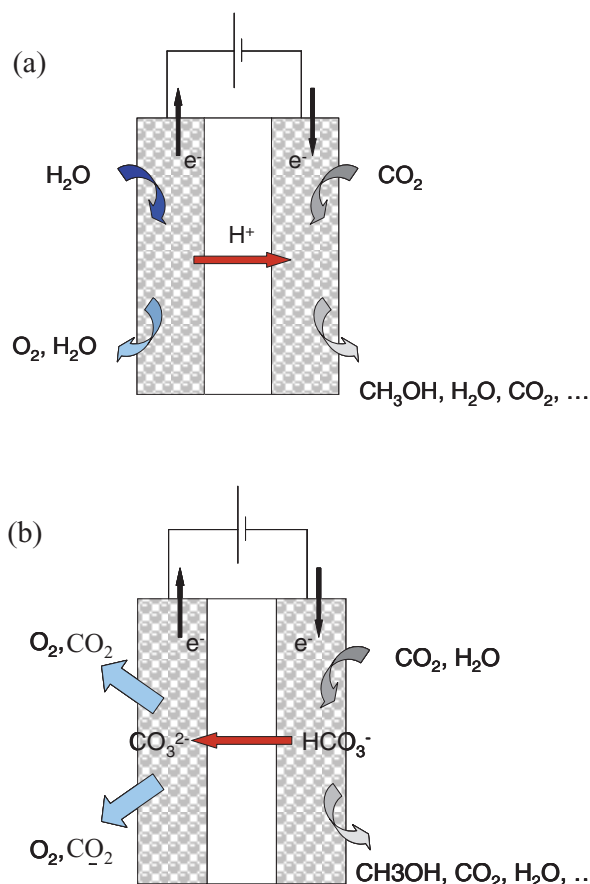


FIG. 10. Schematics of (a) proton conducting electrolyte and (b) immobilized aqueous  $\text{KHCO}_3$  electrolyte based electrochemical cells that combine  $\text{H}_2\text{O}$  electrolysis and  $\text{CO}_2$  fixation into hydrocarbons.

placement of a reference electrode near the center of the electrolyte layer.

This electrochemical cell holder has been used to separate the  $\text{H}_2$  and  $\text{O}_2$  electrode overpotentials in an AEC with immobilized aqueous KOH electrolyte operating at 250 °C and 42 bars, by making use of a Pt pseudo-reference electrode.<sup>22</sup> Inconel foam was used for the  $\text{H}_2$  electrode and Ag activated Ni foam for the  $\text{O}_2$  electrode. Figure 9 shows the i-V characteristic of the full cell, as well as the  $\text{H}_2$  and  $\text{O}_2$

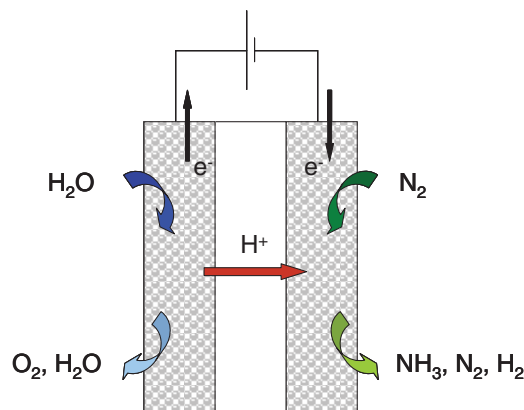


FIG. 11. Schematic of an electrochemical cell that combines  $\text{H}_2\text{O}$  electrolysis and  $\text{N}_2$  fixation into  $\text{NH}_3$ .

TABLE III. Results from the testing of the CB.

Conditions		Feed			Off-gas			
T (°C)	P (bar)	N <sub>2</sub> (Nml/min)	H <sub>2</sub> (Nml/min)	O <sub>2</sub> (Nml/min)	H <sub>2</sub> _expect (Nml/min)	H <sub>2</sub> _MS (Nml/min)	O <sub>2</sub> _expect (Nml/min)	O <sub>2</sub> _MS (Nml/min)
25	1	500 ± 10	50 ± 5	5–10	25–45	35	0	0
25	1	500 ± 10	30 ± 5	5–10	5–25	10	0	0
100	1	500 ± 10	50 ± 5	5–10	25–45	32	0	0
100	1	500 ± 10	30 ± 5	5–10	5–25	9	0	0
200	1	500 ± 10	50 ± 5	5–10	25–45	35	0	0
200	1	500 ± 10	30 ± 5	5–10	5–25	23	0	0
25	10	500 ± 10	50 ± 5	5–10	25–45	36	0	0
25	10	500 ± 10	30 ± 5	5–10	5–25	8	0	0
25	50	500 ± 10	50 ± 5	5–10	25–45	39	0	0
25	50	500 ± 10	30 ± 5	5–10	5–25	10	0	0

electrode overpotentials versus the standard hydrogen electrode (SHE).

### C. Future perspective

Although all the experimental examples presented here are associated with the development of high temperature and pressure AECs, work is carried out in a number of other systems related to the fixation of CO<sub>2</sub> or N<sub>2</sub>. These applications are shortly presented in this section.

#### 1. CO<sub>2</sub> fixation

Co-electrolysis of H<sub>2</sub>O and CO<sub>2</sub> can provide sustainable fuel for the transportation sector, as well as a means of storing electricity from renewable energy sources with large temporal variations. Two types of electrochemical cells that can fix CO<sub>2</sub> into MeOH or other hydrocarbon fuels that are actively pursued by our group are illustrated in Figure 10. The first one (Figure 10(a)) is based on the use of a proton conducting electrolyte and our efforts are directed towards the use of solid acids. An alternative cell based on the use of immobilized aqueous KHCO<sub>3</sub> as electrolyte (Figure 10(b)) is also pursued.

Increasing the operating pressure is desired in order to enhance the thermodynamic stability of the fuel and permit operation at temperatures of 100–300 °C, which is expected to promote the cell performance due to thermal activation of the involved processes. Elevated pressure is also expected to enhance the electrode kinetics, due to the increased impinging frequency and kinetic energy of the reacting gas molecules on the active sites.

#### 2. N<sub>2</sub> fixation

As already mentioned in the Introduction, an electrochemical cell that combines N<sub>2</sub> and H<sub>2</sub>O into NH<sub>3</sub> and O<sub>2</sub> (Figure 11) could help reduce the environmental cost of the Haber-Bosch process. A great challenge here is to identify an electrolyte with high proton conductivity at intermediate temperatures and under dry conditions. Dry N<sub>2</sub> is re-

quired in order to minimize the fraction of active sites for N<sub>2</sub> fixation that will be blocked by adsorption of H<sub>2</sub>O. Since the equilibrium partial pressure of NH<sub>3</sub> decreases with increasing temperature, the operating temperature of such a device may not exceed 300–400 °C. Pressurized operation will improve the thermodynamic stability of NH<sub>3</sub> and the reaction kinetics. Our efforts focus on the development of electrolytes with the desired properties and electrocatalysts for N<sub>2</sub> fixation, using BaZr<sub>1-x-y</sub>Ce<sub>x</sub>Y<sub>y</sub>O<sub>3-δ</sub> (BCZY) based electrolytes.

### ACKNOWLEDGMENTS

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### APPENDIX A: TEST OF CATALYTIC BURNER

As described in the main text, two CBs are installed inside the autoclave, in order to achieve combustion of H<sub>2</sub> and O<sub>2</sub> at room temperature. The CB was tested at 25, 100, and 200 °C at 1 bar, and at 10 and 50 bars at 25 °C, by quantifying the H<sub>2</sub> and O<sub>2</sub> concentration in the off-gas using MS. The results are summarized in Table III. H<sub>2</sub>\_expect is the expected flow rate of H<sub>2</sub> in the off-gas, assuming 100% conversion of the feed H<sub>2</sub> and O<sub>2</sub>. H<sub>2</sub>\_MS is the flow rate of H<sub>2</sub> estimated on the basis of the MS signal. As can be seen in Table III, the H<sub>2</sub>\_MS falls within the limits of the H<sub>2</sub>\_expect in all cases. Furthermore, all the O<sub>2</sub> feed is consumed, as would be expected for 100% conversion since excess H<sub>2</sub> was used in all cases. Finally, the temperature of the CB did not increase by more than 15 °C in any case. According to the manufacturer, the CB should not exceed a temperature of 800 °C. These

TABLE IV. Risk assessment.

Incident/failure	Consequence	Safety system response
Leakage from connections, valves, MFCs, etc. inside the GHC	Possibility of having explosive or toxic gas mixtures in the GHC	The ventilation flow rate is large enough to dilute any possible leakage of explosive gases to levels that are below 15% of the LEL. Furthermore, if the concentration of explosive or toxic gases exceeds 10% of the LEL or the hygienic limit, the gas detectors in the GHC will trigger the safety unit.
Power failure	The gas sensors will be inactive and the furnace temperature will drop to room temperature	A power failure to the safety unit will interrupt the 24 V dc supply to the MVs. The normally closed MVs will shut off the main gas supply to the test station. As the furnace power is shut off, the autoclave will remain cold. The autoclave will be vented since the PCV is normally open.
Power return after power failure	The power to the safety unit, the MVs, the MFCs, the furnace, and the PCV will be restored	The safety unit is programmed such that it will be in safety mode after power-up. The furnace and gas supply will remain shut off until the operator manually resets the safety unit by pressing the “reset” button.
Unintentional addition of H <sub>2</sub> to the autoclave while being filled with O <sub>2</sub> (or the reverse)	Formation of an explosive gas mixture in the autoclave	No automated safety response. Prior to change of gas from O <sub>2</sub> to H <sub>2</sub> (or vice versa), the autoclave must be vented and flushed with an inert gas for at least 50 min!
Ventilation system failure accompanied by leakage from connections, valves, MFCs, etc. inside the GHC	Possible dangerous gas mixtures in the GHC or in the laboratory	If the concentration of explosive or toxic gases exceeds 10% of the LEL or the hygienic limit, the gas detectors in the GHC will trigger the safety unit. Even if the autoclave is filled with pure H <sub>2</sub> at the maximum pressure of 100 bars and all the gas leaks into the GHC (i.e., venting of the autoclave also fails, and the autoclave sealing fails as well), the H <sub>2</sub> concentration in the GHC will remain just below the LEL, as the autoclave gas will be diluted in the volume of the GHC.
Sparks inside the GHC in proximity to explosive gases	Potential ignition source for flammable/explosive gasses	If the concentration of explosive gases exceeds 10% of the LEL, the gas detectors in the GHC will trigger the safety unit. Furthermore, all gas handling components in proximity (distance of 90 cm) to a potential leak of explosive gases (MFCs, valves, pipes, and the PCV) are EX-approved. The autoclave heating jackets are the only exception to this, but they will be powered off in this event.
Pressure controller failure	Pressure in the autoclave will possibly increase. Possible autoclave break-down.	The pressure sensor will trigger the safety unit which will set the system to safety mode once the pressure increases above 99 bars; the gas supply and power to the autoclave furnace will be shut off. Furthermore, the autoclave is equipped with a pressure relief valve which fully opens at 100 bars.
Formation of explosive mixtures of H <sub>2</sub> and O <sub>2</sub> by electrolysis of H <sub>2</sub> O during cell testing	Possible formation of explosive gas mixtures in the autoclave	The autoclave is equipped with two CBs which will recombine the H <sub>2</sub> and O <sub>2</sub> formed during electrolysis into H <sub>2</sub> O. The functionality of the CBs has been carefully examined (Appendix A). The operating temperature of the catalytic burners is monitored to ensure that it stays below 800 °C.
Fire in the laboratory	Possible break down of PLC and safety unit. Possible heat up of the autoclave.	The fire alarm will trigger the PLC and shut off the gas supply to the GHC. If the PLC breaks down the system will be set to safety mode.

results verify that the CB performs adequately well within the temperature and pressure conditions that are employed in the test station.

## APPENDIX B: RISK ASSESSMENT

The following Table IV lists a number of possible incidents in the test station, their potential consequences, and the response of the safety system.

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